8-1975

Fibrous Filler as an Extender for Titanium Dioxide – Methods of Filler Addition

James G. Shaner
Western Michigan University

FIBROUS FILLER
AS AN EXTENDER
FOR TITANIUM
DIOXIDE
-METHODS OF FILLER
ADDITION

by
James G. Shaner

A Thesis Submitted To The
Faculty of the Department of Paper Science
And Endgineering in Partial FUlfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan
August, 1975

ABSTRACT

The paper industry today faces higher costs in such fillers as titanium dioxide. The need for extenders to add to the pulp slurries with titanium dioxide is ever increasing. The extender must not lower the strength properties of the paper to any large extent and must yield nearly the same optical properties as titanium dioxide. Fibrous filler has proven to be a filler which meets these requirements. There exists, however, several different methods for the addition of the fillers to the pulp stock. Each of these methods give different results in the final sheet of paper. It was found from this project that adding titanium dioxide first or while precipitating out the fibrous filler with the total amount of pulp gave the highest optical properties. This is because of one of two reasons. Fibrous filler, while precipitating, increases the retention of the other fillers present. The other reason is that when titanium dioxide is present along with the fibers while fibrous filler is precipitating, something happens in the filler orientation which causes a difference in the way the light rays are scattered in the paper. Fibrous filler when used as an extender can therefore be used to partially eliminate some of the titanium dioxide at a cost savings.

TABLE OF CONTENTS

HISTORICAL BACKGROUND

Fillers are substances which are added to pulp to improve the final sheet of paper. The process of adding mineral matter to the sheet is an old idea. At first it was thought to be bad practice to use fillers. Now, however, if the sheet does not have filler in it, the sheet is considered to be inferior to other papers.

Some of the improvements that are a result of adding fillers are an increase in brightness and opacity, a smoother paper, an increase in ink receptivity and printability, and an increase in density of the paper. Other improvements are an improved appearance and absorbency of the paper, and a decrease in strike-through or show-through of the sheet.

If an excess of filler is used in the making of paper, certain disadvantages result. These disadvantages are a decrease in strength of the paper, a decrease in sizing efficiency, a decrease in pick resistance, and an increase in dusting. Fillers also affect beating, flow properties, web drainage, sheet formation, wire and felt life, calendering, drying and pitch control.

Old fillers were prepared by mechanical methods from natural minerals such as gypsum, chalk, talc and clay. Now fillers are made by a combination of mechanical and chemical means and exist in a wide range. Some fillers in use today are clay, titanium dioxide, barium sulfate, calcium sulfate, calcium carbonate, calcium silicate, talc, diatomaceous silica, zinc oxide, and zinc sulfide. The price range varies from cheap, low grade clays to expensive titanium pigments. Clay and calcium carbonate are the most widely used fillers today with titanium dioxide being the most important filler.

The properties that a filler should have are a high degree of whiteness, a high index of refraction, small particle size (preferably half the wave length of light), low solubility in water, low specific gravity, chemically inert, good retention, and low cost.

Fillers are added to the pulp at many different points in the papermaking process. Filler can be added to the beater, stock chest, fan pump, or even at the wire. Each of these addition points is a result of different optical and retention theories. The filler can be added in dry form or slurry form. If the filler is in slurry form, the filler is easier to handle and can be screened before addition to remove grit and other impurities.

Calcium silicate, when made in situ with the pulp stock, is called fibrous filler. Fibrous filler was developed by R. T. Vanderbilt Company, Inc. Calcium silicate, when made without the pulp stock being present, is called hydrated calcium silicate. Fibrous filler consists of both organic and inorganic components. The filler is made of extremely fine hydrous calcium silicate particles precipitated on specially prepared cellulose fibers. Fibrous filler usually has a composition of eighty percent calcium silicate and twenty percent fiber (1). Because of this strong attachment of filler to fiber, fibrous filler has good retention. The calcium silicates (fibrous filler and hydrated calcium silicate) are spherical in shape with the individual particle size of around 0.07 micrometer. The calcium silicates, however, do not usually act as individual particles, the particles tend to collect into aggregates of 0.2 to 0.3 micrometers. The exact size of the aggregates depends on the preparation procedures. These aggregates are the optimum size for high optical properties.

The refractive index of the calcium silicates is around 1.50. This is not a high refractive index filler, yet it acts like one (high optical properties). There are several reasons for the high optical properties. The filler particles do not act individually, they aggregate to form clusters that form the optimum size of 0.2 to 0.3 micrometers which is half the wave length of light. The silicate pigments are less dense than most other pigments so therefore, in equal weight loadings, the silicates will have a much greater surface for light scattering than the denser fillers. The final reason for the high optical properties of the calcium silicates is because of the "tendency for attachment to the fiber and the alignment of the particles along fiber surfaces. There is, in effect, a spacing of the fibers from each other which brings about improved light scattering and reflectance (2)."

The advantages of calcium silicate in a sheet of paper are high brightness, high opacity, increase in bulk, relative low cost, low abrasion, high ink absorbency, reduced ink strike-through or show-through, good surface smoothness, improved softness, no adverse effects on rosin sizing (3), and good retention by itself and can be used to improve the retention of other fillers in that paper.

A difference of opinion exists on the effect of calcium silicate on paper strength properties. W. V. Arvold (4) and J. P. Casey (5) state that calcium silicates have an adverse effect on tensile, pick, mullen, and fold properties while R. K. Mays (6) states that at the addition levels used in the paper industry, there is no adverse effects on the strength properties.

The disadvantages are loss of strength (according to W. V. Arvold and J. P. Casey), the formation of highly corrosive sodium chloride during the making of fibrous filler in situ (7), and a buildup of soft scale on the inside of the pipe system of the paper mill (8). According to F. H. Denham, several mills used fibrous filler in situ without washing the filler and fibers and have experienced no trouble with production due to the sodium chloride (9). Because of the soft scale buildup, the mill pipe system should be cleaned at regular intervals. Because of the refraction index of calcium silicate being in the same range of cellulose, calcium silicate is not used in the manufacture of grades such as waxing, greaseproof, or glassine paper. Also because of the low refraction index, calcium silicate is not used as a complete replacement for the high refractive index fillers (10).

Calcium silicate pigments can be purchased in either dry or slurry form, or can be made in situ at the mill at a savings in cost. Hydrated calcium silicate (dry filler) disperses in water to a lump free slurry that is slow settling. If the filler is used in dry or slurry form, it can be added to the pulp stock at three different locations. The locations are the beater, fan pump, or on the wet web. Between the beater addition and the fan pump addition, the addition at the fan pump works best for the highest paper properties (11). The addition of filler at the fan pump will mix the pigment internally in the paper and will have the best effect for printability. Adding the pigment at the wet web will yield higher retention.

When the calcium silicate pigment is made in situ at the mill (fibrous filler process), the process is carried on in the beater or refiner.

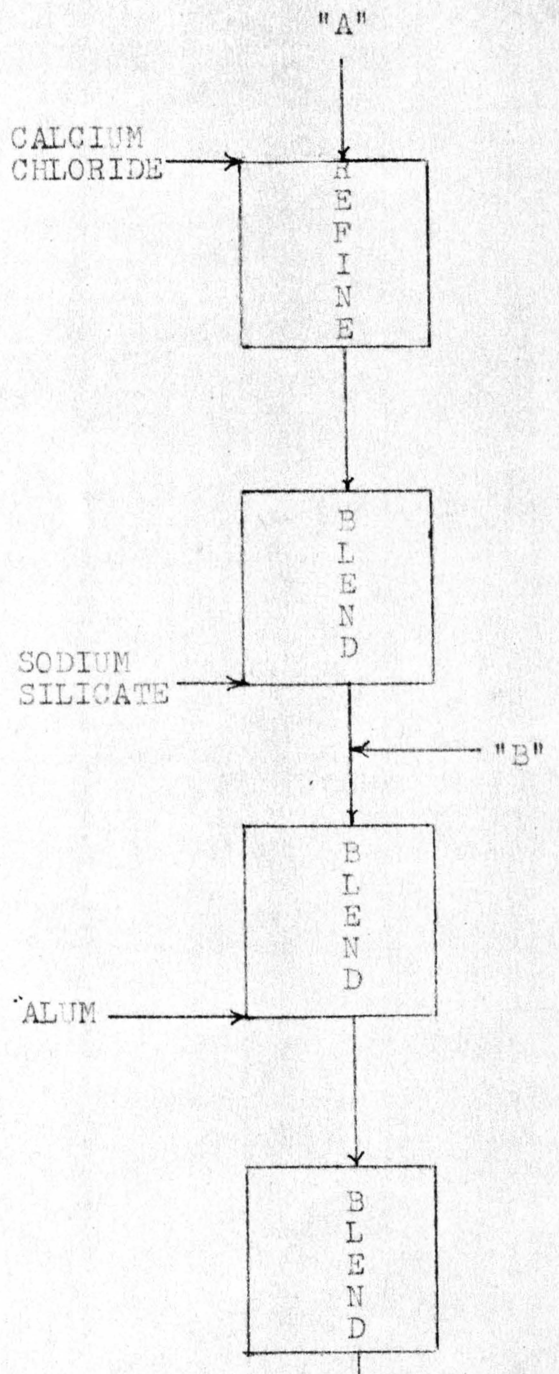
Fibrous filler is made by refining the three percent consistency stock after adding a ten percent solution of calcium chloride, maximum fibrillation being desired. The stock is refined to 350 milliliters Canadian Standard Freeness. A ten percent solution of sodium silicate is then added to the above mixture under high shear agitation and mixed for thirty minutes. After this step, an alum solution is added to the pulp stock under high shear agitation again. Refining the stock along with calcium chloride and creating as much fibrillation as possible causes the fibers to be soft and swelled. This tends to promote better filler attachment to the fibers. Sodium silicate is added under high shear agitation because this produces a finely divided precipitate on the fiber. The addition of calcium silicate, if too rapid or not under high shear agitation or if in a concentration of more than twenty five percent, will yield a gel. This gel is undesirable. Alum is used to reduce the pH of the stock from 10.3 to 4.5 or 5.0. Alum is used for this purpose because mineral acids will dissolve the filler and will reduce the pigment yield. The alum reacts with the pigment to form a complex hydrous calcium aluminum silicate. This step will also increase the pigment yield by twenty percent. Reducing the pH is necessary to bring the stock pH down to where the sizing will not be adversely affected. The soluble salts that are formed as byproducts can be removed by washing (12, 13, 14).

Even though the fibrous filler had a high pH before neutralization, the calcium silicate fillers are not considered alkaline fillers. When an acid pH has been established using alum in a furnish, there is no reversion to the neutral or alkaline condition. The pH can be lowered with alum without foaming or other difficulties. Theoretically, it takes .75 parts alum to 1 part calcium silicate. In practice, however, it takes less alum (15).

Calcium silicate filler is used as an extender for more expensive fillers at a considerable savings in cost. It takes roughly 2.5 parts of silicate filler to equal 1 part titanium dioxide in optical properties (16). When not used as an extender, calcium silicate is added in amounts of three to six percent of the furnish. The synthetic, silica fillers can be used in such paper grades as bond, offset, mimeo, and even fine writing papers. The silica fillers can also be used in various grades of paperboard.

FIGURE 1

Filler Addition Procedure



JUSTIFICATION AND OBJECTIVE

Titanium dioxide is a filler that yields high brightness and high opacity. The cost of titanium dioxide is, unfortunately, very high. Calcium silicate is a filler with good brightness and opacifing powers and has a relatively low cost compared to titanium dioxide. Therefore, the use of calcium silicate as an extender for titanium dioxide should lower the cost of filling the paper while maintaining the same optical properties of titanium dioxide. Other advantages of using calcium silicate as an extender for titanium dioxide are an increase in bulk, high ink absorbency, low abrasion, and better retention of the combined fillers. The disadvantage of using calcium silicate as an extender for titanium dioxide is that the making of calcium silicate in situ yields a highly corrosive sodium chloride as a byproduct.

The objective of this study was to determine the optimum method of the addition of calcium silicate, as an extender for titanium dioxide, to the pulp stock. The optimum method of addition was determined by the strength and optical properties that each experiment yielded.

EXPERIMENTAL PROCEDURE

The first part of this experiment consisted of making the pulp and filler slurry. The second part consisted of making handsheets and testing them.

The pulp used in this project consisted of 50 percent Esponola softwood kraft and 50 percent Weyerhaeuser hardwood kraft. The pulp stock had a consistency of two percent. The titanium dioxide used was rutile titanium dioxide. The pulp was refined, mixed, blended, and agitated in a Valley beater. The handsheets were made on a Noble and Wood handsheet machine.

The filler addition levels were based on the oven dry fibers. Since 2.5 parts of fibrous filler can be used to replace 1 part of titanium dioxide (see historical background) for optimum conditions at a cost savings, this was the ratio used.

Pulp Preparation

A brief description of the manufacture of calcium silicate fibrous filler is as follows (see Figure 1):

(1) Refine the three percent consistency fiber stock in the presence of calcium chloride to 325 Canadian Standard Freeness.

(2) After thirty minutes of agitation, add

sodium silicate to the above under conditions of rapid agitation. Blend for thirty minutes.

(3) Adjust the pH of the above to neutral with alum again under conditions of rapid agitation.

Twelve different methods of filler addition were completed in this project.

Experiment 1 "No Filler" Using the Valley beater, the two percent consistency pulp stock was refined to about 325 Canadian Standard Freeness (CSF). The pulp was then agitated for one hour.

Experiment 2 "Fibrous Filler-with total pulp" The procedure on the preceding page was followed with an addition level of fibrous filler being 12.5 percent of the oven dry stock.

Experiment 3 "Titanium Dioxide Filler-with total pulp" Again using the Valley beater, the two percent consistency stock was refined to 325 CSF. Titanium dioxide was then added at an addition level of five percent. This pulp and filler mixture was then blended for thirty minutes.

Experiment 4 "Fibrous Filler and Titanium Dioxide-with total pulp" Following the procedure in Figure 1, add titanium dioxide to the pulp at point "A". The addition level of titanium dioxide was 2.5 percent and the addition level of fibrous filler was 6.25 percent of the oven dry stock.

Experiment 5 "Fibrous Filler and Titanium Dioxide-with total pulp" Following the procedure in Figure 1, add titanium dioxide to the pulp at point "B". The addition level of titanium dioxide was 2.5 percent and the addition level of fibrous filler was 6.25 percent of the oven dry stock.

Experiment 6 "Fibrous Filler and Titanium Dioxide-with total pulp" Following the procedure in Figure 1, add titanium dioxide to the pulp at point "C". The addition level of titanium dioxide was 2.5 percent and the addition level of fibrous filler was 6.25 percent of the oven dry stock.

Experiment 7 "Fibrous Filler-with part of pulp" The amount of calcium silicate filler needed for an addition level, to the total pulp, of 12.5 percent was first calculated. A pulp and filler slurry containing 80 percent calcium silicate and 20 percent fiber was then prepared using the calculated amount of calcium silicate. The procedure in Figure 1 was followed using a blender for all refining and mixing. The rest of the pulp was agitated in the Valley beater. Finally the pulp in the blender was added to the pulp in the beater and agitated for thirty minutes in the Valley beater.

Experiment 8 "Fibrous Filler and Titanium Dioxide-with part of pulp" The amount of calcium silicate filler and titanium dioxide needed for addition levels, to the total pulp, of 6.25 and 2.5 percent respectively were first calculated. A pulp and filler slurry containing 80 percent filler and 20 percent fiber was then prepared using the calculated amount of fillers. The procedure in Figure 1 was followed with the addition of titanium dioxide at point "A". A blender was used for all refining and mixing. The rest of the pulp was agitated in the Valley beater. Finally the pulp in the blender was added to the pulp in the beater and agitated for thirty minutes in the Valley beater.

Experiment 9 "Fibrous Filler and Titanium Dioxide-with part of pulp" This experiment was the same as Experiment 8, except titanium dioxide was added to the slurry at point "B" in Figure 1.

Experiment 10 "Fibrous Filler and Titanium Dioxide-with part of pulp" Again, this experiment was the same as Experiment 8, except titanium dioxide was added to the slurry at point "C" in Figure 1.

Experiment 11 "Hydrous Calcium Silicate and Titanium Dioxide" A ten percent solution of sodium silicate was added to a ten percent solution of calcium chloride under agitation and mixed for thirty minutes. The pH of the above was adjusted to neutral with alum under agitation for thirty minutes. The above was filtered and the precipitate was dried. The precipitate was hydrous calcium silicate. The calcium silicate was added to the pulp stock at a level of 6.25 percent and mixed in the beater for thirty minutes. Titanium dioxide was then added to the above stock at a level of 2.5 percent and mixed in the beater for thirty minutes.

Experiment 12 "Titanium Dioxide and Hydrous Calcium Silicate" This experiment was basically the same as Experiment 11, except the titanium dioxide was added first to the pulp with hydrous calcium silicate being added last.

Handsheet Preparation and Paper Tests

The handsheets from the different stocks were made on a Noble and Wood handsheet machine. All of the handsheets were pressed with the same amount of pressure and were dried with a steam heated drum dryer. After conditioning the handsheets for 24 hours, the following tests were made on the paper: tensile, mullen, tear, brightness, opacity, caliper, basis weight, and filler retention. All of these tests were TAPPI standard. The results for the tensile and mullen tests were reported in pounds per square inch. The results for the caliper test were determined from a micrometer and were reported in thousandths of an inch. The basis weight results were in pounds per 25 inch by 38 inch by 500 sheet ream. The filler retention was determined by ashing a known amount of paper in an oven at 1400 degrees Fahrenheit. The ash weight was then corrected for filler loss through ignition. Since titanium dioxide did not lose any weight when ignited, the correction factor that the ash weight had to be multiplied by was 1, while the correction factor for Fibrous filler was 1.10. The results were reported as retention of filler and percent filler in paper.

DATA AND DISCUSSION

Optical Properties

The optical tests were brightness and opacity. Some pulps gave good brightness while at the same time giving low opacity and vice versa. The pulps in which titanium dioxide was added either before fibrous filler or while fibrous filler was precipitating in the total pulp (Experiments 4 and 5) gave the highest optical properties. This was because of one of two reasons.

TABLE I

Brightness and Opacity

EXP. NO.	1	2	3	4	5	6	7	8	9	10	11	12
BR.	73.6	78.6	76.8	77.9	78.7	75.9	76.5	72.1	75.8	76.4	77.3	77.4
OP.	74.1	79.9	77.5	79.9	78.2	76.7	77.3	78.9	79.2	79.1	78.7	78.9
RET.		15.8	4.9	13.3	3.7	2.7	7.4	4.3	1.0	13.4	9.5	16.3

Fibrous filler, while precipitating, usually increases the retention of the other fillers present (see Historical Background). If the titanium dioxide was added after the fibrous filler was precipitated, then the retention should not be as high. Experiments 4 and 5 in TABLE I both had titanium dioxide present when the fibrous filler was precipitating while Experiment 6 had titanium dioxide added after the fibrous filler was precipitated. It can be seen that both Experiments 4 and 5 had a higher retention than Experiment 6.

The other possible reason why Experiments 4 and 5 had the highest optical properties was that when titanium dioxide is present along with the fibers while fibrous filler is precipitating, something happens in the filler orientation which causes a difference in the way the light rays are scattered in the paper (see Historical Background). Experiments 8, 9, and 10 had the fillers added to only part of the pulp and then mixed with the remainder of the pulp. Experiments 11 and 12 had the fibrous filler precipitate without the fibers being present and then added to the pulp. All of these experiments (8,9,10,11, and 12) caused a different filler and fiber orientation than Experiments 4 and 5 had. From TABLE I it can be seen that this difference in filler and fiber orientation caused a difference in optical properties..

Bulk Property

To test the bulk of the paper, the caliper test was used. The pulp in which no filler was added had the lowest bulk while the pulps which contained both fibrous filler and titanium dioxide had the highest bulk. These results are given in TABLE II. The reason for this increase in bulk

TABLE II

Caliper

EXP. NO.	1	2	3	4	5	6	7	8	9	10	11	12
CAL.	5.4	5.5	5.5	5.6	5.6	5.5	5.6	5.7	5.7	5.8	5.7	5.7

was that the fillers, when attached to the fibers, caused the fibers to become further separated when they bond so that the thickness of the paper increases. Thus if no filler was added, as in Experiment 1, the bulk of the paper is at its minimum while the rest of the experiments, which have fillers present, show an increase in bulk.

Strength Properties

The strength properties of the paper were determined from the tensile, mullen, and tear tests. The "No Filler" stock (Experiment 1) had the highest tensile and mullen values while the weakest paper was made from the pulp in which the hydrous calcium silicate was added in dry form along with titanium dioxide (Experiments 11 and 12). The data for the strength properties are given in TABLE III. The reason why the fillers decrease the tensile and mullen tests was that when the filler particles attached to the fibers, they took up fiber area and hence decreased the amount of fiber to fiber bonding. When there existed less actual fiber to fiber bonding, the strength of the paper goes down.

TABLE III

Strength Tests

EXP NO.	1	2	3	4	5	6	7	8	9	10	11	12
TEN	8.5	7.4	7.8	7.5	7.3	8.4	7.7	8.0	7.4	7.5	7.2	7.0
MUL	25.7	23.4	24.5	23.5	22.3	25.5	24.4	24.1	21.5	24.1	20.4	17.8
TEAR	43.5	45.7	47.6	47.4	52.4	45.6	49.2	50.0	55.4	46.2	46.2	44.6

Again from TABLE III, it is obvious that the tear test of the experiments that had fillers in them (Experiments 2 through 12) went up. Since filler particles were bonding to the fibers, more friction exists between the fibers when the paper was torn. This means that more force is needed to pull the fiber out of the sheet of paper, hence a higher tear value.

CONCLUSIONS

From this work, several conclusions can be made. The procedure of either adding titanium dioxide first or while fibrous filler is precipitating in the total amount of pulp yields the highest optical properties with good bulk while not reducing the strength properties to any large extent. The pulps in which the fillers were added in a small amount of pulp first and then mixed with the total amount of pulp have more bulk, and slightly lower strength and optical properties when compared to the paper made from pulps in which the fillers were added to the total amount of pulp. Paper made from pulps containing hydrous calcium silicate in dry form and titanium dioxide had fairly good optical properties but lowered the strength properties severely.

In summary, the best procedure for adding fibrous filler and titanium dioxide is to either add titanium dioxide first or while fibrous filler is precipitating in the total amount of pulp.

TABLE 4

Summary Of Data

EXP NO.	% FILL.	RET.	TEN.	MULLEN	TEAR	BRIGHT	OPAC	CAL.	B. WT
1	X	X	8.5	25.7	43.5	73.6	74.1	5.4	44.20
2	0.79	15.8	7.4	23.4	45.7	78.6	79.9	5.5	43.13
3	0.61	4.9	7.8	24.5	47.6	76.8	77.5	5.5	42.00
4	1.16	13.3	7.5	23.5	47.4	77.9	79.9	5.6	42.92
5	0.34	3.7	7.3	22.3	52.4	78.7	78.2	5.6	42.31
6	0.24	2.7	8.4	25.5	45.6	75.9	76.7	5.5	42.16
7	0.65	7.4	7.7	24.4	49.2	76.5	77.3	5.6	42.95
8	0.38	4.3	8.0	24.1	50.0	72.1	78.9	5.7	42.49
9	0.09	1.0	7.4	21.5	55.4	75.8	79.2	5.7	43.78
10	1.17	13.4	7.5	24.1	46.2	76.4	79.1	5.8	43.49
11	0.83	9.5	7.2	20.4	46.2	77.3	78.7	5.7	44.39
12	1.42	16.3	7.0	17.8	44.6	77.4	78.9	5.7	43.18

1= No Filler 2= Titanium Dioxide 3,7= Fibrous Filler
4,5,6,8,9,10,11,12= Fibrous Filler and Titanium Dioxide
FOR FURTHER EXPLANATIONS ON THE EXPERIMENTS, SEE "EXPERIMENT PROCEDURE."

LITERATURE CITATIONS

1. Denham, F.H., Tappi 38, No. 7:115A, (July 1955).

2. Brooks, A.M., Tappi Monograph Series, No. 19:52, Tappi, (1958).

3. Brooks, A.M., Tappi Monograph Series, No. 19:52, Tappi, (1958).

4. Arvold, W.V. and Calott, P., Tappi 39, No. 11:823, (1956).

5. Casey, J.P., Pulp And Paper, 2nd edn., New York, Interscience, 1960, vol. 2, p. 985.

6. Mays, R.K., "Synthetic Silica And Silicate Fillers," Report given at Panel Discussion on Special Additives, Canadian Pulp and Paper Association Technical Section, Canada, (Jan. 22, 1963).

7. Schwalbe, H.C., Pulp And Paper Manufacture, 2nd edn., New York, McGraw-Hill, 1970, vol. 3, p. 19.

8. Arvold, W.V. and Calott, P., Tappi 39, No. 11:823, (1956).

9. Denham, F.H., Tappi 38, No. 7:115A, (July 1955).

10. Mays, R.K., "Synthetic Silica And Silicate Fillers," Report given at Panel Discussion on Special Additives, Canadian Pulp and Paper Association Technical Section, Canada, (Jan. 22, 1963).

11. Arvold, W.V. and Calott, P., Tappi 39, No. 11:823, (1956).

12. Craig, W.L., Tappi Monograph Series, No. 19:42, Tappi, (1958).

13. Denham, F.H., Tappi 38, No. 7:115A, (July 1955).

14. Arvold, W.V. and Calott, P., Tappi 39, No. 11:823, (1956).

15. Brooks, A.M., Tappi Monograph Series, No. 19:52,

16. Brooks, A.M., Tappi Monograph Series, No. 19:52, Tappi, (1958).

REFERENCES

1. Allen, E.M., "Method Of Preparing A Siliceous Pigment," U.S. pat. 2,865,777 (July 6, 1955).

2. Arvold, W.V. and Calott, P., "The Preparation And Use Of Fibrous Filler In The Paper Mill," Tappi 39, No. 11:823 (1956).

3. Berndt, W., "Silicate Fillers," Papiermacher 20, No. 6:92 (1970).

4. Bertorelli, O.L., "Preparation Of Crystalline Silicate Acid Pigments," U.S. pat. 3,110,606 (Nov. 12, 1963).

5. Bertorelli, O.L., "Silicate Pigments," U.S. pat. 2,739,073 (Sept. 6, 1950).

6. Brooks, A.M., "Calcium Silicate," in "Paper Loading Materials," Tappi Monograph Series No. 19:52, Association Of The Pulp And Paper Industry (1958).

7. Calkin, W.S., "Modern Pulp And Paper Making," 3rd edn., New York, Reinhold Publishing Corp., 1957, p. 294.

8. Callahan, J.W., "Evaluation Of Mineral Opacification Agents For Printing Papers," Tappi 50, No. 11:96A (1967).

9. Casey, J.P. "Pulp And Paper," 2nd edn., New York, Interscience, 1960, vol. 2, p. 985.

10. Craig, W.L., "Calcium Silicate-Fibrous Filler," in Paper Loading Materials," Tappi Monograph Series No. 19:42 Association Of The Pulp And Paper Industry (1958).

11. Davidson, R.R. "Experiments On Loading Paper With Low Refractive Index Fillers," Paper Technology 6, No. 2:107 (1965).

12. Denham, F.H., "Fibrous Filler-A New Pigment For The Paper Industry," Tappi 38, No. 7:115A (1955).

13. Gandon, L., "Synthetic Silicates And Their Preparation," British pat. 1,039,940 (Aug. 24, 1966).

14. Higham, R.R.A., "Basic Notes On Materials Used As Fillers And Loadings In Papermaking," Paper And Printing 33, No. 3:341 (1960).

15. Ivanov, S.N. and Kuznetskii, V.V., "Calcium Silicate As Paper Filler," Bumazh. Prom., No. 10:12 (1970).

16. Ivanov, S.N. and Kuznetskii, V.V., "Preparation Of Artificial Silicate Filler," Bumazh. Prom., No. 10:9 (1968).

17. Lagerstrom, G.B., "Process For The Production Of Siliceous Pigment," British pat. 907,156 (Oct. 3, 1962).

18. Lagerstrom, G.B., "Siliceous Pigments For Paper, Process For Their Preparation, And Treated Papers," French pat. 1,264,512 (May 15, 1961).

19. Mays, R.K., "Filler Pigments: State Of The Art," Tappi 53, No. 11:2116 (1970).

20. Mays, R.K., Williams, L.E., and Geffken, C.F., "Surface Of Newsprint As Viewed By The Inkmaker," Tappe 53, No. 11:2129 (1970).

21. Mays, R.K., "Synthetic Silica And Silicate Fillers," Report given at Panel Discussion on Special Additives, Canadian Pulp and Paper Association Technical Section, Canada, (Jan. 22, 1963).

22. Mays, R.K., "The Synthetic Silicas And Silicates As Paper Fillers," Report submitted to J.M. Huber Corp., Maryland, U.S., (March 12, 1964).

23. Podschus, E. and Kollmann, O., "Use Of A Calcium Silicate Pigment As A Filler For Brightening Paper," German pat. 977,011 (Nov. 5, 1964).

24. Polovinkin, V.L. and Lapin, V.V., "Influence Of Silicate Fillers On Characteristics Of Printing Paper," EUCEPA Conference, Paper Printability (Budapest) 14, Paper No. 12 (Oct. 1971).

25. Postauk, P. and Ancelle, B., "Influence Of Fillers And Pigments On The Opacity And Show-Through," ATIP Bulletin, No. 6:279 (1964).

26. Samaryanova, M.B. and Koval'chuk, N.F., "Synthetic Fillers For Paper," Bumazh. Prom., No. 9:7 (1970).

27. Schwalbe, H.C., "Fillers And Loading," in "Pulp And Paper Science And Technology," 1st edn., New York, McGraw-Hill, 1962, vol. 2, p. 60.

28. Schwalbe, H.C., "New Developments In The Loading Of Paper," Paper Trade Journal 139, No. 11:32 (1955).

29. Seve, R., "Phenomena Of Light Scattering; The Classical Theory And Its Application To The Opacity Of Papers," ATIP Bulletin 18, No. 6:255 (1964).

30. Schwalbe, H.C., "Nonfibrous Material," in "Pulp And Paper Manufacture," 2nd edn., New York, McGraw-Hill, 1970, vol. 3, p. 19.

31. Swanson, J.W., "The Science Of Chemical Additives In Papermaking," Tappi 44, No. 1:142A (1961).

32. Taylor, L.B., "Calcium Silicate-Filled Paper," U.S. pat. 3,190,789 (June 22, 1965).

33. Willets, W.R., "Introduction" in "Paper Loading Materials," Tappi Monograph Series No. 19:1 Association Of The Pulp And Paper Industry (1958).

34. Willets, W.R., "Titanium Dioxide And Other Pigments," in "Handbook Of Pulp And Paper Technology," 2nd edn., New York, Van Nostrand Reinhold, 1970, p. 605.